

University of Alberta Library



0 1620 3069129 7

## For Reference

---

**NOT TO BE TAKEN FROM THIS ROOM**

Ex LIBRIS  
UNIVERSITATIS  
ALBERTENSIS







Digitized by the Internet Archive  
in 2018 with funding from  
University of Alberta Libraries

<https://archive.org/details/detonation00legg>

1943  
#1A

A THESIS

Detonation

by

N. R. Legge, B.Sc.

University of Alberta

April 21, 1943.



A Thesis

"Detonation"

Submitted in Fulfillment

of the

Requirements for the Degree of

Master of Science

by

N. R. Legge, B.Sc.

Under the Direction of

Dr. J. L. Morrison

Edmonton, Alberta.

April, 1943.



The author wishes to express his gratitude to:

Dr. J. L. Morrison for his generous advice and assistance.

The MacLean Bursary Fund and the University of Alberta Research Scholarship Fund for financial help.

The National Research Council for apparatus and financial assistance.

The Department of Chemistry for laboratory space and facilities.



Table of Contents.

	Page
I. Introduction.....	1
II. Theories of Initiation and Detonation...	4
1.The Wave Synchronism Theory .....	4
2.Berthelot's Theory .....	4
3.The Energy Chain Theory .....	5
4. The Tribo-Chemical Theory.....	8
5. The Breaking Theory .....	9
III. The Testing of Explosives .....	12
IV. Description of Apparatus and Experimental Procedure.....	16
1.The Sand Test .....	16
2.The Friction Test .....	16
3.The Impact Test .....	20
V. Experimental Results and Discussion .....	24
VI.A Discussion of Theory .....	49
VII.A Summary of Proposed Experiments .....	58
VIII. Bibliography .....	60



## INTRODUCTION

Davis (1) describes an explosion as "a loud noise and a sudden going away of things from the place where they have been." An explosive is defined as "a material, either a pure single substance, or a mixture, which is capable of producing an explosion by its own energy."

There are three types of explosives:

- (1) Primary or initiating explosives, which explode by the application of heat or from impact or friction. An example is mercury fulminate.
- (2) Secondary or high explosives which must be exploded by the shock from an initiating explosive. For example -- trinitrotoluene.
- (3) Propellants -- substances, usually mixtures which, upon the application of heat or the shock from an initiating explosive give a steady rise of pressure. An example is gunpowder.

Initiating explosives do not generally have a melting point. They explode before melting. The explosion points of most lie in a range from 150° C



to 350° C. They are very sensitive to impact and to friction.

With increasing use of explosives there arose the problem of accidental explosions during handling. As a result, the testing of explosives was started. Berthelot, Dautriche, Wohler, Abel and others measured velocities of detonation, impact sensitiveness, heat sensitiveness and other properties.

The initiating ability of explosives was found to vary. Too large amounts of mercury fulminate were required to detonate the new nitro explosives. Mixtures of mercury fulminate with potassium chlorate were better. These mixtures, with added substances, are still used in small caps. However, most of the new mixtures proved to be very susceptible to shock and blows. To avoid such mixtures boosters may be used. These are substances, such as tetrinitrophenyl-methyl nitramine (tetryl), which are somewhat more sensitive to the action of an initiator than ordinary high explosives. They are interposed between the initiator and the high explosive to transmit the energy efficiently.

Various theories of the initiation and detonation of explosives have been proposed. However, all have



been rather unsatisfactory. Most explosive data is unreliable and difficult to reproduce.

It is hoped to develop a satisfactory theory of detonation based on reliable experimental observations. Such a theory would assist in the designing of new initiators and high explosives. Incidental to obtaining experimental data it was necessary to design impact and friction sensitiveness apparatus. These may also be valuable in the commercial production and handling of explosives.



## THEORIES OF INITIATION AND DETONATION

### Wave Synchronism Theory

Abel, as quoted by Colver (4), advanced the hypothesis of wave synchronism. It ascribes the action of the primary explosive to be due to its wave synchronism, or sympathetic molecular vibration, with that of the secondary explosive. The explosives, he assumed, were tuned to a certain explosive wave exactly as in acoustics. Berthelot criticised the theory, pointing out that action in the case of the two explosives should be reciprocal. Further, every explosive should then show wave synchronism with itself and be the perfect igniter for itself. However, it has been shown that with mercury fulminate and other initiators, dynamite is sometimes left partly unexploded. On the other hand, in the case of cast explosives such as T.N.T. and picric acid, the same explosive interposed loosely between the detonator and the cast explosive will result in the detonation of the latter.

### Berthelot's Theory of Detonation

Berthelot (3,4) considered that detonation of an explosive is caused by a percussive wave. By rapid adiabatic compression the temperature of succeeding layers of explosive is raised to the decom-



position point. The adiabatic compression theory is well founded in the case of gaseous explosions. However, Nernst (5) doubts its validity for solids.

[ Taylor and Weale (6) calculated the energy required to explode a mercury fulminate mixture by impact. Assuming that the total energy of the blow reached the mixture and was converted into heat, the temperature of the mixture would be raised 20° C. The explosion temperature of the mixture was 163° C. The actual energy reaching the explosive in the system would be much less than the calculated amount.]

#### The Energy Chain Theory

This theory was advanced by Muraour (7). It is based on the classification of explosives into two groups.

- (1) Those in which the combustion wave, in free air, is transformed instantaneously, or almost so, into a detonation wave with a velocity of several thousand metres per second.
- (2) Those in which the combustion wave, in free air, has a velocity of only a few centimetres per second. This wave is not transformed into a detonation wave.

Initiators generally fall into the first class and high explosives into the second.



The exceptional velocity of combustion of detonators is explained by the formation of energy chains. When an explosive molecule is decomposed part of its energy is available for the activation of neighboring molecules. As a result of resonance phenomena one or several of the neighboring molecules can receive, in one way only, the total energy required for their activation. These molecules in the same manner activate some neighboring molecule. Thus the energy is passed rapidly across the solid mass, independent of the gaseous pressure. If one considers the formation of branched chains (a molecule in decomposing activates two or more molecules) then the velocity of reaction can become extremely great.

Muraour observes that a shock wave is necessary to start an explosive wave. This shock may be from an initiator or from the combustion of an explosive under high density. In the latter case an extremely rapid growth of pressure, approaching a shock, is produced. This creates a mechanical compression wave which is maintained by decomposition of successive layers of explosive. If the explosion already has a high velocity of combustion in free air (i.e. it is an initiator), then the iner-



tia of the gaseous mass released can be great enough to start the explosive wave.

Muraour has tabulated and examined the properties of many explosives. A brief resume of his conclusions is of some interest.

Heats of formation -- Most initiating explosives are endothermic. When an endothermic molecule is decomposed the heat of reaction is immediately available. When an exothermic molecule is decomposed the energy of reaction is only produced by the subsequent reaction of the atoms and molecules of the original decomposition. The velocity of reaction in the first case would be much greater. A few initiators, such as lead picrate, hexamethylenetriperoxideamine and tricycloacetone are exothermic.

Temperature of Decomposition -- has no effect on the ease with which the combustion wave is transformed into a detonation wave. Cyanuric triazide and tetryl have the same temperature of decomposition.

Comparison of other characteristics -- The velocity of detonation is markedly lower for initiating explosives than for secondary explosives. The force per unit volume calculated for mercury fulminate is high, but for other initiating explosives it is of the same order or lower than those of secondary explosives.



Examination of Chemical Formulae -- The presence of heavy metal seems to increase the possibility of an explosive being an initiator. Muraour assumes that the presence of the heavy metal favors the formation of the energy chains. The initiators with structures having only a small number of bonds seem to be more efficient. This may be explained by Polanyi's theory. The energy furnished to a molecule on heating distributes statistically between the different bonds. As a result of interfering phenomena, it may accumulate at a certain moment on a bond and the bond will rupture. If the molecule is complex the probability of the energy accumulating in a single bond is small.

The Tribu-Chemical Theory

Taylor and Weale (6,8) have done some very accurate and interesting work on explosives. They consider the processes of initiation and detonation may be explained on the basis of tribu-chemistry.

The forces involved in the impact explosion of initiators and in the detonation of high explosives are large. Under these very intense pressures the crystals of explosive are subjected to normal stresses and tangential shearing. The former tend to bring the surface molecules into very intimate contact and



the latter to break these contacts. The continued process of surface linkage and disruption results in the chemical decomposition of the medium at a velocity which is proportional to the rate at which work is being done in the process. To this may be added the thermal reaction and the effect of the hot gases liberated. If these combined processes reach a critical value the action becomes self-propogative, i.e. the detonation wave commences.

In their second paper (8) Taylor and Weale deduce some pressure-time relationships. For mercury fulminate they found that an impulsively applied pressure of over 7 tons per square inch may cause complete detonation in less than  $10^{-5}$  seconds.

#### The Breaking Theory of Detonation

In two long papers (9) Carl has submitted the breaking theory of detonation. The papers are very interesting both from a practical and theoretical viewpoint. A brief discussion of the theory follows.

Detonation is a progressive breaking of the valence bonds of a material, by a stress which is transmitted through the material as an elastic wave. This may be considered as a sound wave of such intensity as to destroy the structure of the material.



The breaking wave is maintained by the release of gases and heat from the explosive. Thus it is a continuous compression. Its passage through the explosion will be affected by the elasticity of the medium. The optimum condition is then perfectly elastic material which requires only a slight distortion to cause a breakage of its bonds.

The sensitivity of endothermic compounds and of exothermic compounds is assumed to be quite different, the former being more sensitive. Both types have external weakness -- surface unsaturation -- while one, the endothermic compound, has inherent internal weakness. This latter is like the internal strain discussed by von Baeyer.

[However, as Muraour has pointed out, some very sensitive initiators are exothermic.]

Carl states also that increased crystal size causes increased sensitiveness in endothermic compounds. He bases this on the observation that large crystals of lead azide have exploded without warning. This idea is quite widely received.

[On the other hand, Miles (10) has grown crystals of lead azide 3 centimetres or more in length which



could be crushed safely with a spatula. Miles attributes any increased sensitiveness of large crystals to distortions in the crystal structure. When this occurs the energy of the structure will be much higher than usual.]

The explosive will be less sensitive to detonation if there is present any agency, force or quality which protects or supports the crystal or molecule or which tends to prevent transmission of stresses by elastic waves. A few such agencies are: a resistant container, high density of charge, mutual support by intertwined crystals, toughness, colloidal dispersion of explosives, addition of coating material.



TESTING OF EXPLOSIVES

(1) The Temperature of Explosion -- is important in any practical use of explosives. The method generally is to drop successive small portions of explosive on the surface of a heated Wood's metal bath or melting point block. The temperature is raised at a steady rate until a fresh portion of the sample explodes or deflagrates. Methods using glass tubes and only one portion of sample are unreliable.

There is an induction period before explosion takes place. This period is shorter as the temperature is raised. At the explosion temperature recorded, there should be an induction period of 5 seconds, or less.

(2) Hot Wire Ignition -- This is a preliminary test to the sand test. A short resistance wire is surrounded by an explosive. The wire is raised to a red heat, or exploded, by an electric current. If the sample detonates it may be used alone in the sand test. Otherwise an initiator must be used. The test is also useful as an igniter in determining whether an initiator deflagrates or detonates in free air.



(3) Power Tests -- There are several methods :-

- (a) the sand test (4,11)
- (b) the Trauzl expansion test (4)
- (c) the ballistic mortar (4)
- (d) the Hopkinson pressure bar (12,13).

The sand test is the simplest and has the widest application. The explosive is loaded into a small metal (aluminium) detonator shell. It may be packed loosely or pressed to a known density. A sulfur plug containing an iron resistance wire is placed in the shell. The wire protrudes slightly so that it is in contact with the explosive. The top of the shell is crimped and molten sulfur poured in to fill and seal it. The steel bomb has a cylindrical cavity  $6 \times 1\frac{1}{4}$  inches. The cover has two small holes for the electrical firing wires. The cavity is half filled with standard Ottawa sand (20-30 mesh). The detonator shell is placed in an upright position in the centre of the cavity. Then the bomb is filled with sand and the cover clamped on. The amount of sand is previously weighed. After firing the explosive electrically the bomb is taken apart. The sand is screened through 30, 60, 100 mesh screens after removing any metal fragments. The weight of sand on each screen is recorded. The weight of sand crushed smaller than 30 mesh is a measure of the power of the explosive.



The test may be used for the power of initiators, their ability to initiate high explosives, and the power of high explosives.

(4) The Friction Test -- The usual friction test apparatus (14,18) consists of a curved shoe which swings over a concave anvil. The explosive is placed on the anvil. The pendulum is raised to a position on a scale and released. The number of swings required to detonate the explosive is determined.

The "Dupont tester" is used to give an indication of the sensitiveness of an explosive to a glancing blow. A hard steel torpedo slides down inclined rails and strikes the explosive placed on a steel anvil. Thus the explosive is subjected to a glancing impact.

(5) The Impact Test -- Perhaps the most important test is that of sensitiveness to impact. Yet impact data are the most unreliable of all explosive data.

A layer of explosive is placed between two hard steel surfaces and subjected to an impact. The impact is from a falling weight and is transmitted by the upper plate or column. There are many designs of apparatus (4,6,12,14, 15).

The sensitiveness of an explosive to impact is dependent upon:



- (a) its explosive properties
- (b) its physical state
- (c) the amount used
- (d) the area of contact of the impacting surface
- (e) the shape of the confining surfaces
- (f) the hardness of the confining surfaces
- (g) the degree of confinement (pressure, density)
- (h) the striking weight used
- (i) the height of fall of the weight
- (j) the elasticity and shape of the weight
- (k) the rigidity of the system.

There may be other factors. The failure to record more than h, i, and perhaps c and d is the main reason for the unreliability of impact results.

In determining sensitiveness to impact a statistical method (6) must be used. At least 20 trials should be made at each height for a given weight. The heights should be selected to give a range of explosions from 10 to 90%. The height for 50% explosions of 20 trials is generally taken as the critical height.



## DESCRIPTION OF APPARATUS AND EXPERIMENTAL PROCEDURE

(1) The Sand Test -- The apparatus was made according to specifications from Colver (4). Some details of dimensions are given in the Appendix Figure 1.

The detonator shells were of aluminium 4.7 centimetres long and 0.53 centimetres in diameter. The resistance wire of the plugs was 30 gauge standard iron wire. Sulfur plugs were made up in the laboratory using sections of detonator shells as moulds. The Ottawa standard sand was within the limits of 20 to 30 mesh.

The explosives were weighed accurately after pressing to a recorded pressure in the shell. The sand was weighed to the nearest decigram before and after the trial. The current used was such that the resistance wires were exploded. All the exploded shells were placed in envelopes and labelled.

(2) The Friction Test -- The usual friction test was considered unsatisfactory. The "Dupont tester" involves impact as well as friction. A satisfactory test of the sensitiveness to "pure" friction was desirable.

Dr. Kendrick of the University of Toronto reported a preliminary apparatus consisting of two steel plates with explosive between clamped in a hydraulic vise.



One of the plates was struck on an end with a hammer to produce the frictional effects.

It was decided to build a friction apparatus with a known moving force and with the friction between the moving plate and the load eliminated.

Friction Machine Number 1 -- a diagrammatic sketch is seen in Figure 1. The steel pendulum (1) was hung on a bearing. The load was applied to the plates (2) and (3) by a roller (4). Besides easy revolution, this roller was able to move only in a vertical direction. The plates were of mild steel.

The operation of the apparatus was as follows :-  
The plates were polished on grade 0 emery paper and carefully wiped. About 1 milligram of explosive was dusted on the lower plate so that it was directly under the applied load. The upper plate was placed on top, protruding to the point of rest of the pendulum. The load was applied by lowering the roller. The pendulum was drawn back to a position on the scale and released. The impact forced the upper plate over the lower plate. The pendulum was allowed a follow-through of 1 centimetre, where it was bounced back by a rubber stop. The plates were examined microscopically after each trial.

The resistance offered to the movement of the upper



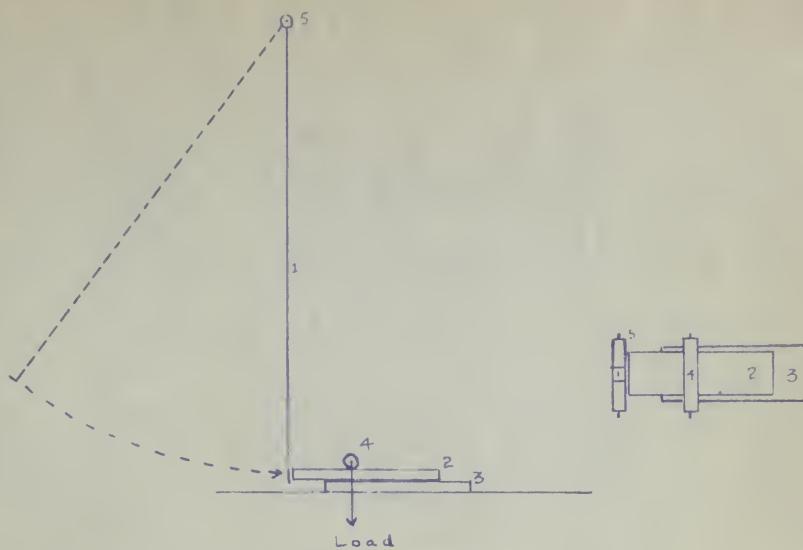


Fig. 1. friction machine No. 1.

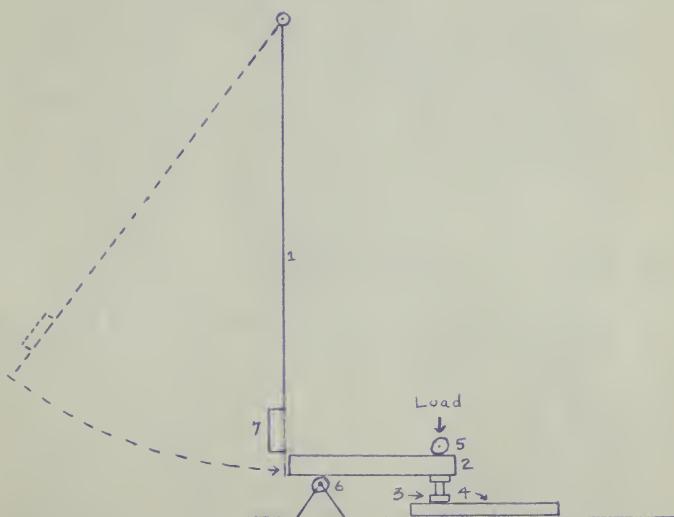


Fig. 2. friction machine No. 2.



Friction Machine No.2.





plate is due to the friction developed between the plates under the load. This frictional effect could be increased by increasing the load and/or the initial velocity of the plate, i.e. by increasing the striking force of the pendulum. If the load and velocity were great enough sufficient frictional effects were developed in the explosive to cause its detonation. The explosion was very audible.

Some difficulties were encountered with this first apparatus. The steel plates were found to be "ploughed" in places. Under the applied load the plates were forced into intimate contact. Bonds or welds were formed between the plates and when the upper plate moved these welds tore or "ploughed" the metal. It was hoped to avoid this by the use of very hard steel plates. However, these were ploughed in the same manner. Plates of plate glass were tried but they shattered when an explosion occurred.

According to Bowden (16) this ploughing effect is a commonplace factor of the friction between two metals. Agreement with Bowden was obtained on the tearing of metals even at low speeds and small loads. The phenomenon occurs with all metals independent of hardness and the only remedy seemed to be effective lubrication. However, as ploughing did not occur in every trial it was decided



to have a few sets of mild steel plates made. Trials in which ploughing occurred were not considered and the plates were polished down when the ploughing was excessive.

As trials proceeded with new plates the number of positive results under given conditions was found to increase with time. Constant results were difficult to obtain. It was suspected that the coefficient of friction between the two plates was varying with the extent of the polish. This was confirmed in the literature (17). The coefficient of friction between two metal plates diminished as the extent of polish increased, reached a minimum at a certain polish and then increased very rapidly. For this reason the design of the apparatus was changed.

Friction Machine Number 2 -- The large upper plate was replaced by a much smaller surface. The effective surface could be covered completely with explosive, avoiding the contact of steel on steel.

Figure 2 is a diagramatic sketch. A more detailed drawing is shown in Figure 2 in the Appendix. The striking system was changed only by the addition of a 5 pound lead weight (7) clamped to the end of the pendulum (1). This weight shifted the center of percussion to the end of the pendulum. The upper plate was the head (3) of a 3/8 inch bolt. The effective surface was 1.35 centimeters



in diameter. The bolt was threaded into a steel bar ② which rested on a roller ⑥ at one end and on the bolthead at the other end. The lower plate ④ was one of the plates of the first apparatus. The load was supplied by a roller ⑤ resting directly above the bolthead.

The trials were carried out in a similar manner to those on the first apparatus. The lower plate was cleaned with a rubber eraser and a cloth. The explosive was dusted on the plate, covering the entire area upon which the bolthead rested. The bar was placed on the roller ⑥ with the bolthead covering the explosive. The roller ⑤ was lowered and the weight attached. Then the pendulum was drawn back and released. Upon impact the bar moved forward over roller ⑥ and under roller ⑤. The surface of the bolthead was always covered with explosive so that there was no contact of steel on steel and no ploughing.

(3) Impact Apparatus -- The design was one used by Kast ④ and modified slightly. There were three main types of systems used.

Type I is shown in Figure 3 and in Figure 3 in the Appendix. The essential parts are the hammer ① and the anvil ②. They are held in place by the outer retainer ③ and the guard ring ④. The base ⑤, a



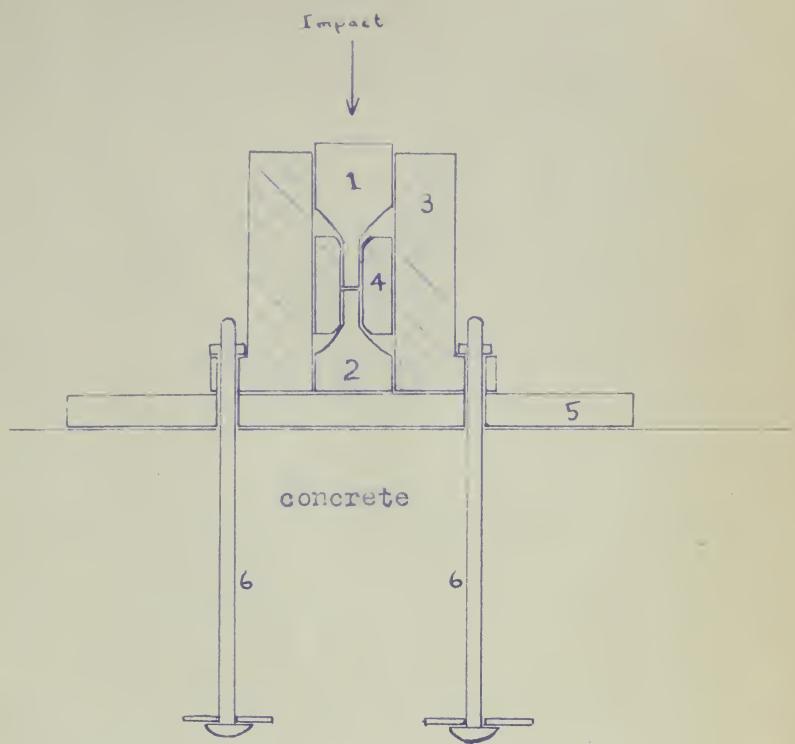


Fig. 2. Impact Apparatus Type I.



$\frac{1}{2}$  inch mild steel plate, was held in place by the rods ⑥ embedded in a concrete block. The hammer and anvil were of hard, heat-treated nickel steel with circular striking surfaces 0,95 centimetres in diameter.

The procedure was as follows: the explosive was dusted in a thin layer on the anvil. The apparatus was assembled and the nuts on the rods ⑥ tightened. By means of a lever arm the charge was pre-pressed to a definite pressure and the pressure released. Then a cylindrical mild steel weight was dropped from a recorded height by an electro-magnet. The hammer and anvil were examined. A positive result (detonation) could be distinguished easily. There was no noise of the explosion.

In preliminary testing only 5 trials were done at each height. Later, 20 trials at each height were found necessary.

The hammer and anvil surfaces were cleaned after each trial by polishing on grade O emery paper. The difficulty of keeping the surface perfectly plane was very great. As a result the effective impact area of the surfaces was roughly 1/10 of the original area.

For trials on sensitive detonators S.K.F. steel balls were substituted for the mild steel weights.



Type II was designed to prevent the hammer from bouncing after impact of the weight.

The system is shown in Figure 4 and in Figure 3 in the Appendix. A flat steel plate (1) rested on the hammer. This plate had a circular opening (2) in the centre enabling the steel ball to strike the hammer directly. The edges of the opening were bevelled to avoid impact of the ball. A lever arm system connected to the plate provided loads from 50 to 300 pounds.

The accuracy of dropping the steel balls was improved. They were suspended electromagnetically from a point surrounded by a rubber ring. Experiments were carried out with hammers and anvils 3/8 inch and 1/4 inch in diameter.

Type III Reproducible results were obtained with Type II only when the impact surfaces remained constant. However, this was found very difficult to do.

Type III apparatus seen in Figure 5 was introduced in hope that the impact surfaces would be reproducible. A steel ball (3) 3/8 inch in diameter was placed between the 3/8 inch hammer (1) and the anvil (2). It fitted closely in the guard ring (4). The pressure plate (5) was retained.

The system was subjected to numerous impacts of



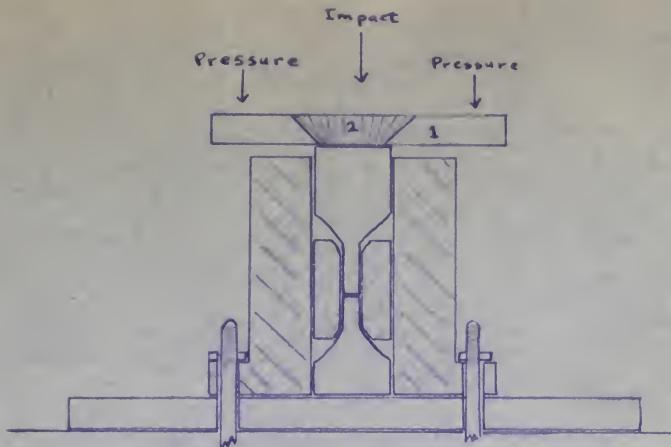


Fig.4. Impact Apparatus Type II.

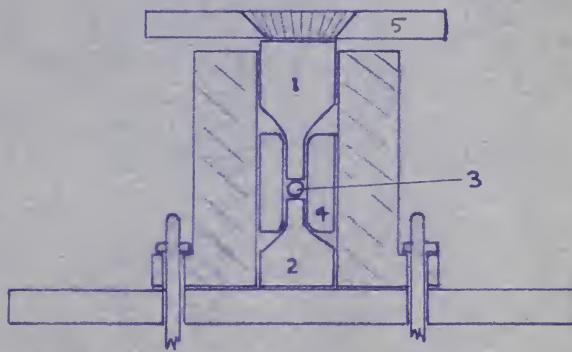
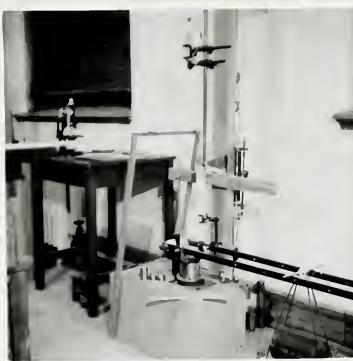


Fig.5. Impact Apparatus Type III.



Type II Impact Apparatus.





one of the larger weights. Circular indentations were produced in the hammer and anvil. After several impacts these cup-shaped indentations became constant in size. The diameter of the indentation in the anvil was measured by a cathetometer and found constant throughout the experiments.

The explosive was dusted evenly in this indentation. The apparatus was assembled and trials carried out as for Type II.



## EXPERIMENTAL RESULTS AND DISCUSSION

### 1. The Sand Test

Some preliminary tests were made on lead azide "unprotected" and "protected" (i.e. sample precipitated in a very dilute gelatin solution). Results are given in Table I.

Table I

<u>Sample</u>	<u>Weight of Sample</u>	<u>Weight of sand crushed</u>
Lead azide (unprot.)	0.3385 gm.	10.81 gm.
Lead azide (unprot.)	0.6577 gm.	22.79 gm.
Lead azide (protected)	0.3294 gm.	11.04 gm.

These results compare well with those obtained by Clark (18) as shown in Figure 6. The same size and type of bomb was used. There may have been slight differences in the type of detonator shell. One result from an initiator test (see Table II) with protected lead azide and T.N.T. is shown in Figure 6. The T.N.T. was not detonated. The result is low because some energy of explosion was used in compressing the T.N.T.



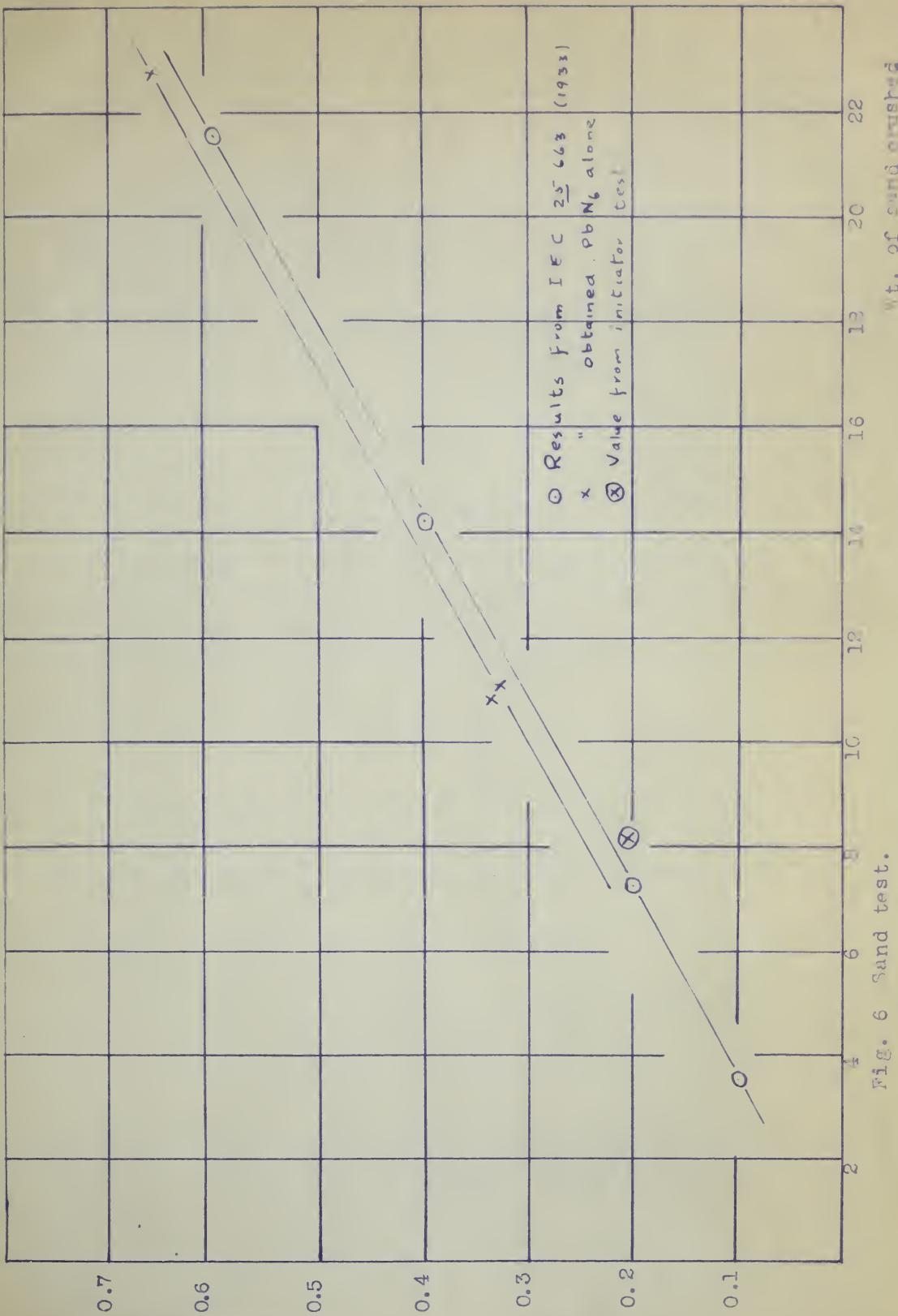


Fig. 6 Sand test.



Initiating Ability of Lead Azide (protected)

T.N.T. was the high explosive used. Results are seen in Table II.

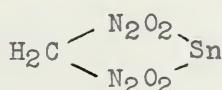
Table II

<u>Weight of Lead Azide</u>	<u>Result</u>
0.1616 gm.	No detonation of the T.N.T. Sand crushed by lead azide.
0.1829 gm.	ditto
0.2064 gm.	ditto, 8.13 gm. of sand crushed.
0.2032 gm.	No detonation of the T.N.T. Sand crushed by lead azide.
0.1672 gm.	Slight decomposition of T.N.T., 10.35 gm. of sand crushed.

Clark (18) reports 0.16 gm. as the minimum detonating charge of unprotected lead azide for T.N.T. Results show protected lead azide to be less powerful than the unprotected type.

Tests on Stannous Methylenedinitramine

Stannous methylenedinitramine was prepared accord-



ing to Robinson and Wright (19). Sand tests of the compound alone and of its initiating ability were carried out. Results are given in Table III and



Table IV.

Table III

Sand Test of Stannous Methylenedinitramine

<u>Weight of sample</u>	<u>Weight of sand crushed</u>
0.4417 gm.	19.14 gm.
0.4463	8.76
0.4415	8.66

The result of the first test could not be duplicated or explained. The other tests show close agreement. Assuming that they are correct the weight of sand crushed is approximately one half that for the same weight of lead azide --- from Figure 6.

Table IV

Initiating Ability of Stannous Methylenedinitramine  
for 0.4 gm. of T.N.T.

<u>Weight of Tin Salt</u>	<u>Result</u>
0.0768 gm.	No deton. of T.N.T.; no sand crushed.
0.1020	ditto
0.1645	ditto
0.2087	ditto
0.2089	ditto
0.2640	ditto



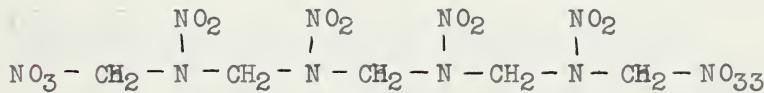
Table IV continued.

<u>Weight of Tin Salt</u>	<u>Result</u>
0.3000 gm.	Only rapid decomposition of tin salt.
0.3450	ditto
0.4006	No detonation of T.N.T.; no sand crushed.
0.3000	ditto

The compound showed no apparent initiating ability. Ignition by a hot wire in open air left an appreciable amount of yellow colored residue. The rapid combustion (similar to a propellant) in the detonator shell was found in other borderline initiators. (See lead methazonate.)

Tests of Stannous Methylenedinitramine as an Initiator  
for Compound 106

A sample of compound 106 was supplied by Dr. G. F.



Wright. Its impact sensitivity was given as 12 x T.N.T.

Three trials were made on 106 initiated by the tin salt. Results are shown in Table V.



Table V

106 Initiated by the Tin Salt

<u>Wt. of Tin Salt</u>	<u>Wt. of 106</u>	<u>Result</u>
0.1007 gm.	0.3821 gm.	106 decomposed not detonated.
0.0995	0.3905	106 unchanged. Tin salt gave rapid combustion only.
0.1136	0.3844	crushed 10.59 gm. sand, i.e. 106 crushed approx. 8 gm.

Compound 106 was tried as a booster between the tin salt and pentaerythritol tetranitrate (P.E.T.N.). However, in two trials the tin salt failed to detonate. In the third trial the tin salt detonated but failed to detonate the 106 or P.E.T.N. These results indicate the unreliability of the tin salt under the conditions of the test.

Tests on the Lead Salt of Methazonic Acid

The lead salt of methazonic acid was prepared

$$\text{HO} - \text{N} = \text{CH} - \text{CH} = \text{NO}_2 - \text{Pb} - \text{O}_2\text{N} = \text{CH} - \text{CH} = \text{N} - \text{OH}$$

according to Dunstan and Goulding (20). The salt is brown colored, exploding with a sharp crack on the melting point block at approximately  $210^{\circ}\text{C}$ .

In the sand test this compound showed no detonating



power. Several times the shells were burst by a slowly increasing pressure. There was no shattering effect (no crushed sand).

Tests on Pentaerythritol tetranitrate P.E.T.N.

P.E.T.N. was prepared in the laboratory by the nitration of pentaerythritol. A sample of technical P.E.T.N. was obtained from Dr. Wright. The two samples were recrystallized by dissolving in acetone and pouring into water. They melted at the same temperature,  $139^{\circ}$  -  $140^{\circ}$  C. The samples were detonated by lead azide in the sand test. A sample containing 5% CdO was tested. Results are given in Table VI.

Table VI

Sand Test of P.E.T.N.

<u>Wt. of PbN<sub>6</sub></u>	<u>Wt. of P.E.T.N.</u>	<u>Sand crushed</u>
0.0825 gm. (prot. PbN <sub>6</sub> )	0.3818 gm. (Prep. recryst.)	36.71 gm.
0.0812 (prot. PbN <sub>6</sub> )	0.3820 (Tech. recryst.)	36.27
0.0730 (unprot. PbN <sub>6</sub> )	0.3830 (Tech. recryst. + 5% CdO)	36.97

The results show the prepared and technical P.E.T.N. to have the same power. The added CdO does not increase the power. The small weight of protected lead azide used shows the sensitiveness of P.E.T.N. to be much



greater than that of T.N.T. (P.E.T.N. is 5 times more sensitive to impact than is T.N.T.)

## 2. The Friction Test

(1) Friction Machine No. 1 -- the compound tested was stannous methylenedinitramine. Several tests were made on lead azide and mercury fulminate but these required loads which caused excessive ploughing. Results of stannous methylenedinitramine are given in Table VII.

Table VII

### Friction Sensitiveness of Stannous Methylenedinitramine.

<u>Load</u>	<u>Horizontal Distance Pendulum</u>	<u>% Fires in 10 Trials</u>
5.62 kg.	60 cm.	30
5.62	65	40
5.62	70	70
5.62	75	90
6.6	35	50
6.6	40	90
6.6	50	90
6.6	60	80

In a critical region, there is a sharp rise in the number of positive results over a small range of



distances on the pendulum. This region drops appreciably as the load is increased. The last result in Table VII is rather out of place. As the error in 10 trials is at least 10% this divergent result is to be expected. The results are more clearly defined than in the impact apparatus.

The relation between load, pendulum distance and percentage positive results is not a simple one.

Preliminary trials on fulminate and lead azide gave results roughly in accordance with their impact sensitivities.

A series of trials was carried out with mild steel plates, omitting trials in which ploughing occurred, and polishing down when ploughing became excessive. Table VIII shows results obtained with the tin salt on a new set of these plates.

Table VIII

Tests using a new set of mild steel plates on Tin Salt.

<u>Load</u>	<u>Horizontal Distance Pendulum</u>	<u>% Fires in 20 Trials</u>
7.2 kg.	50 cm.	90
7.2	40	65
7.2	35	60
7.2	30	70



Table VIII continued.

<u>Load</u>	<u>Horizontal Distance Pendulum</u>	<u>% Fires in 20 Trials</u>
7.2 kg.	30 cm.	80
7.2	30	100
5.8	25	45
5.8	25	40
5.8	35	90

An increase in the frictional effects commences with the third result. With a smaller load an indication of further rise is seen in the last result. These results show the effect of steel on steel friction and the importance of avoiding it.

(2) Friction Machine No. 2 -- The friction of steel on steel is eliminated by this design. Some results are given in Table IX.

Table IX

Results on Friction Machine No. 2.

<u>Compound</u>	<u>Load</u>	<u>Distance Pendulum*</u>	<u>% Firing</u>
Stannous	6.9kg.	25 cm.	60
Methylene-dinitramine	6.9	30	80
Mercury	33.6	50	36
Fulminate	33.6	60	86



Table IX continued.

<u>Compound</u>	<u>Load</u>	<u>Distance Pendulum*</u>	<u>% Firing</u>
Lead	44.6kg.	85	73
Azide (unprotected)			

\* The horizontal distance from the point of rest of the pendulum. Up to 60 cm. this distance is approximately the same as that on Friction Machine No. 1.

As before, these results show a clearly defined critical region. The values for stannous methylenedinitramine are about the same as on Machine No. 1. The friction sensitiveness parallels impact sensitiveness for the three compounds. However, a much wider range of compounds must be used to show that this is a general occurrence.

If the explosion of a sample was due to the generation of frictional heat sufficient to raise a portion of the sample to the explosion point, then the friction sensitivities would parallel the explosion points of the compounds. This is not so. Stannous methylenedinitramine and mercury fulminate have approximately the same explosion temperature (190-200°C.). Lead azide explodes around 330°C.

When a negative result occurred the plates were examined microscopically. For the three compounds tested an "ice" was observed. That is, the crystal-



lites had been forced together by pressure and movement to form a transparent sheet. The phenomenon was called "icing" by analogy to the formation of ice from snow under pressure. This ice only occurred when there was probability of detonation. Below the pressure and force required for positive results icing was not noticeable. The ice appeared the same for all three compounds in their critical regions.

#### Tests of Tracer-Igniter Compositions and Gunpowders

Dr. Downing of the University of Toronto sent ten samples of tracer-igniter mixtures and gunpowders to be tested. They were too insensitive for the range of the present apparatus. Most of the tracer-igniter compounds contained metallic magnesium particles. Microscopic examination showed that these particles prevented the full frictional loading of the crystalline material -- the crystalline material was not compressed or moved. Samples containing these particles of metal will not give satisfactory results in this test unless the pressure greatly exceeds the flow pressure of the metal. The test does show the effect of desensitizing or coating agents on the compounds. One of the samples contained paraffin wax as a desensitizer. When it was tested the plate moved much farther than was usual under the conditions of the test. The wax lubricated the surfaces very efficiently. Samples



containing chlorinated rubber and resins were not protected to such a degree.

### 3. Impact Test.

#### Some Energy Relations in the Impact Test.

Impact test results could be given in different ways, depending on the theory of detonation. Taylor and Weale (6) found that the probability of detonation depended upon the kinetic energy of the falling weight. For a given sample the product of the weight and the critical height (for 50% explosions) was constant for a small range of weights and heights.

They mention that, using mild steel hammers and anvils, much greater energies were required to cause ignitions and smaller weights appear to produce ignitions with less kinetic energies than did larger weights. This was attributed to deformation of the mild steel.

Their criterion for a striking weight is an inelastic mass. The striking weights used were hardened steel balls which are very elastic. Such balls would bounce appreciably. No mention of the bounce was made.

Urbanski (21) attributes the innovation of the determination of the rebound of the falling weight to Wohler and Wenzelberg. Urbanski records the re-



bound height and subtracts it from the original height thus obtaining an effective height.

Powell and Ubbelohde (22) support the view that the probability of explosion is determined by the momentum of the blow. A fraction of this momentum may be lost due to imperfect rigidity of the system.

Dr. Johns, Department of Physics (private communication), suggested that the probability of explosion might be governed by the impulse of the blow and not by the kinetic energy of the weight. The value of impulse is derived as follows:

Impulse = Force x time.

$Ft$  = mass x change in velocity

$Ft$  =  $m(v_1 + v_2)$                                $v_1$  = velocity down  
     $v_2$  = rebound velocity

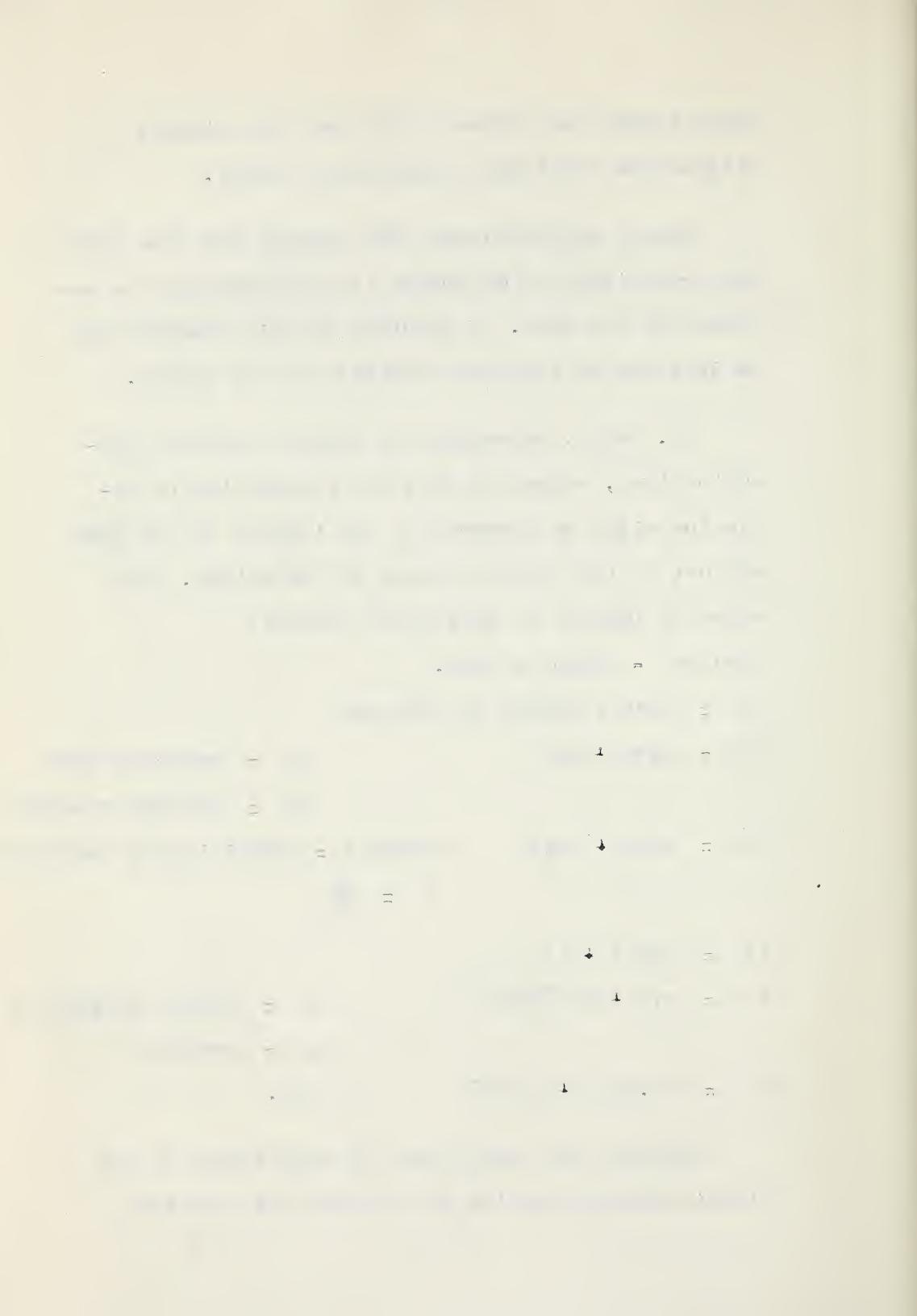
$Ft$  =  $m(v_1 + ev_1)$                               where  $e$  = coefficient of restitution  
     $e = \frac{v_2}{v_1}$

$Ft$  =  $mv_1(1 + e)$

$Ft$  =  $m(1 + e)\sqrt{2gh}$                                $h$  = height of fall  
     $g$  = gravity

$Ft$  =  $44.3m(1 + e)\sqrt{h}$                               (i).

Applying the coefficient of restitution in the kinetic energy equation one obtains the relation



$$\begin{aligned} \text{K.E.} &= \frac{1}{2}mv^2(1 - e^2) \\ &\approx mgh (1 - e^2) \quad (\text{ii}). \end{aligned}$$

The equations (i) and (ii) were used in calculating the impulse and kinetic energy.

(a) Type I Impact Apparatus

The apparatus as first constructed had a suitable range for high explosives as well as initiators.

The first tests were made on a basis of the height for no explosions in five trials. The compounds were generally pre-pressed to approximately 2000 pounds per square inch. In this preliminary work the extent of pre-pressing was not very important.

Dr. G. F. Wright had mentioned the effect of cadmium salts in sensitising high explosives such as P.E.T.N. It was hoped to sensitise high explosives into an initiator range. Results of tests on some initiators, high explosives, and mixtures are given in Table X.

The added substances had a definite sensitising effect on P.E.T.N. The metals were the most efficient sensitisers. However, the sensitisation is not enough to bring the high explosive into the range of initiating explosive.



Table X

Maximum Weight x Height for No Explosions in 5 Trials.

(Weight -- mild steel cylinder)

<u>Material</u>	<u>Weight X Height</u>
Mercury fulminate	3.2 kg. cm.
Lead azide	8.9
P.E.T.N.	81.3
R.D.X.	204.0
T.N.T.	> 320.0
P.E.T.N. - 2% CdO	42.3
" - 5% CdCl <sub>2</sub>	33.0
" - 5.5% CdBr <sub>2</sub>	38.0
" - 6% CdI <sub>2</sub>	35.5
" - 2% Cd metal	12.0
" - 5% Sb metal	12 approx.

Since there is a statistical spread in the probability of explosion 5 trials were not enough. Twenty trials were found more satisfactory. Lead azide, protected and unprotected; mercury fulminate, and stannous methylenedinitramine were tested. The results are given in Table XI and plotted in Figure 7.

The tin salt is the most sensitive of the compounds tested. The protected lead azide was found to be more



sensitive than the unprotected sample. This is contrary to accepted results. However, the sensitivities of the two types are close together (22).

Table XI

<u>Substance</u>	<u>Weight x height</u>	<u>% Firing</u>
Stannous methyl-enedinitramine	3.2 kg. cm.	12.5
"	3.6	15
Mercury fulminate	3.2	2.5*
"	3.6	12.5*
"	3.8	55
"	7.6	85
"	11.5	85
Lead azide (prot.)	10.2	20*
"	20.3	35*
"	30.5	48*
"	40.7	80*
Lead azide (unprot.)	20.3	22.5*
"	30.5	25
"	40.7	40
Compound 106	25.4	27.5

\* -- 40 Trials.

The "Bounce Effect" -- In testing the stannous methyl-enedinitramine it became necessary to use a smaller weight. A 28.1 gm. S.K.F. steel ball ( $\frac{3}{4}$  inch diameter) was used. As the tests proceeded it was noticed that, when the small ball bounced back on the hammer, the



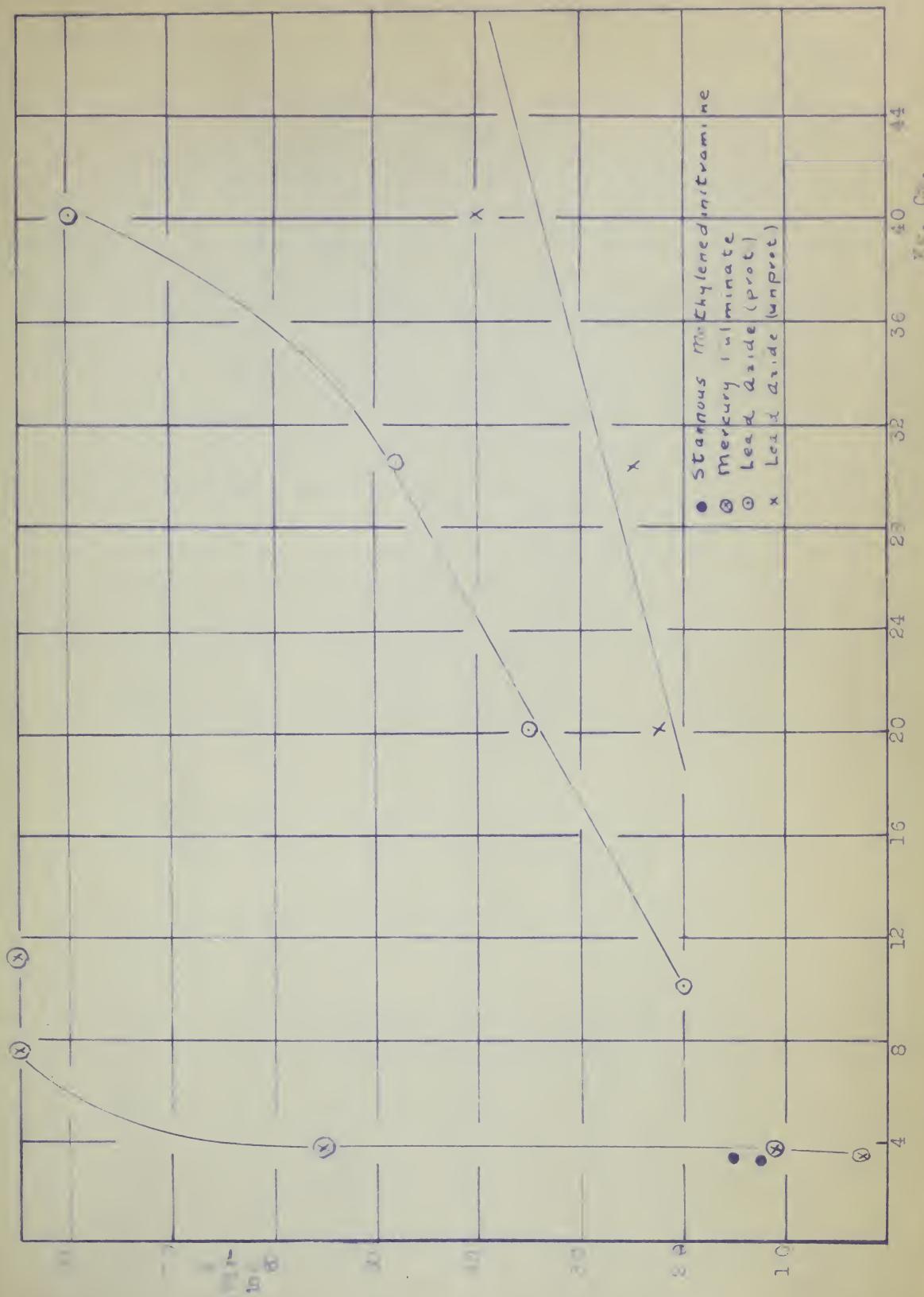


FIG. 7.



result was usually positive. Twenty trials were made catching the ball after impact. Then 20 trials were made in which the ball was forced by a paper collar to strike the hammer again after bouncing. The results were as follows:-

No bounce striking 28.1 gm. wt., 127 cm. -- 15% Firing.  
All bounces striking 28.1 gm. wt., 50 cm. -- 75% Firing.  
Therefore the bounce of the falling weight is very important in impact tests. (This work done before obtaining references 21, 22.)

Further trials were carried out to determine whether the bounce effect was due to an activation of the explosive by the first blow. Results are shown in Table XII.

Table XII  
The Bounce Effect

<u>Stannous methylenedinitramine</u>						
<u>Weight</u>	<u>Height</u>	<u>Bounce</u>	<u>K. E.</u>	<u>Impulse</u>	<u>% Firing</u>	
28.1 gm.	60 cm.	No	$1.1 \times 10^6$ #	$1.5 \times 10^4$ #	15%	
28.1	100	No	$1.9 \times 10^6$	$2.0 \times 10^4$	25	
28.1	40	All	$1.1 \times 10^6$	$1.8 \times 10^4$	40	
28.1	60	All	$1.7 \times 10^6$	$2.0 \times 10^4$	45	
28.1	80	All	$2.2 \times 10^6$	$2.4 \times 10^4$	85	
<u>Mercury fulminate</u>						
66.6	115	No	$6.7 \times 10^6$	$4.2 \times 10^4$	18.2*	
28.1	115	All	$3.2 \times 10^6$	$2.8 \times 10^4$	20*	



x -- 80 trials each.

# -- C.g.s. units, total for "all bounces".

A definite activation effect is shown. This hardly seems to be explained by a "resonance" phenomena as suggested by Carl (9). The time between impacts is of the order of 0.4 seconds. In several trials the ball bounced out of the retaining collar. It was picked up and dropped from the approximate height of bounce. A positive result was obtained in most cases. The time between impacts in this case would be about 1 second.

(b) Type II Impact Apparatus

The compounds tested were more sensitive with this system (under pressure) than with Type I apparatus. This is shown in Table XIII.

Table XIII

Stannous methylenedinitramine

<u>Type Apparatus</u>	<u>Weight</u>	<u>Height</u>	<u>% Firing</u>
I	28.1 gm.	100 cm.	25
II	28.1	125	75
I	66.6	115	40
II	66.6	80.5	90

Lead azide

I	225	120	0
II	225	75.7	50



The sensitiveness also varied with the load on the hammer and anvil during impact. Some indication of this is seen in Table XIV.

Table XIV

Variation of Probability of Detonation of Lead Azide

With Load.

225 gm. Wt. from 75.7 cm.

<u>Load</u>	<u>% Firing</u>
136 lbs.	37%
228	45
318	15

The percentage increases with load to a maximum then decreases at higher loads. Further tests were made on Type III apparatus.

The 3/8 inch diameter hammer and anvil which had been used became too short for Type II apparatus. A new  $\frac{1}{4}$  inch diameter set was made. It was very difficult to make the impact surfaces perfectly flat and keep them so. Cleaning on emery paper after each trial produced rounded ends in spite of precautions. Results became quite irregular as the surface changed. Therefore, Type III apparatus was used.

(c) Type III Impact Apparatus

The diameter of the circular indentation in the



anvil was 0.238 cm. This value remained constant throughout all the trials with Type III apparatus.

Trials were made on stannous methylenedinitramine. The load on the hammer was varied with constant falling weight and height. The results are shown in Table XV and plotted in Figure 8.

Table XV

Variation of Probability of Detonation with Load

Type III Apparatus

66.6 gm. from 119.4 cm. -- 20 trials.

<u>Load</u>	<u>Coeff. of restitution</u>	<u>% Firing</u>
59.4 lbs.	0.348	20%
74.2	0.380	20
73.5	0.382	20
98.0	0.383	40
98	0.383	40
137	—	35
137	0.383	45
182	0.380	40
182	0.383	40
227	0.389	20
227	—	10

The values of the coeff. of restitution are given to show their small variation, i.e. the energy exchange is fairly constant. The curve in Figure 8



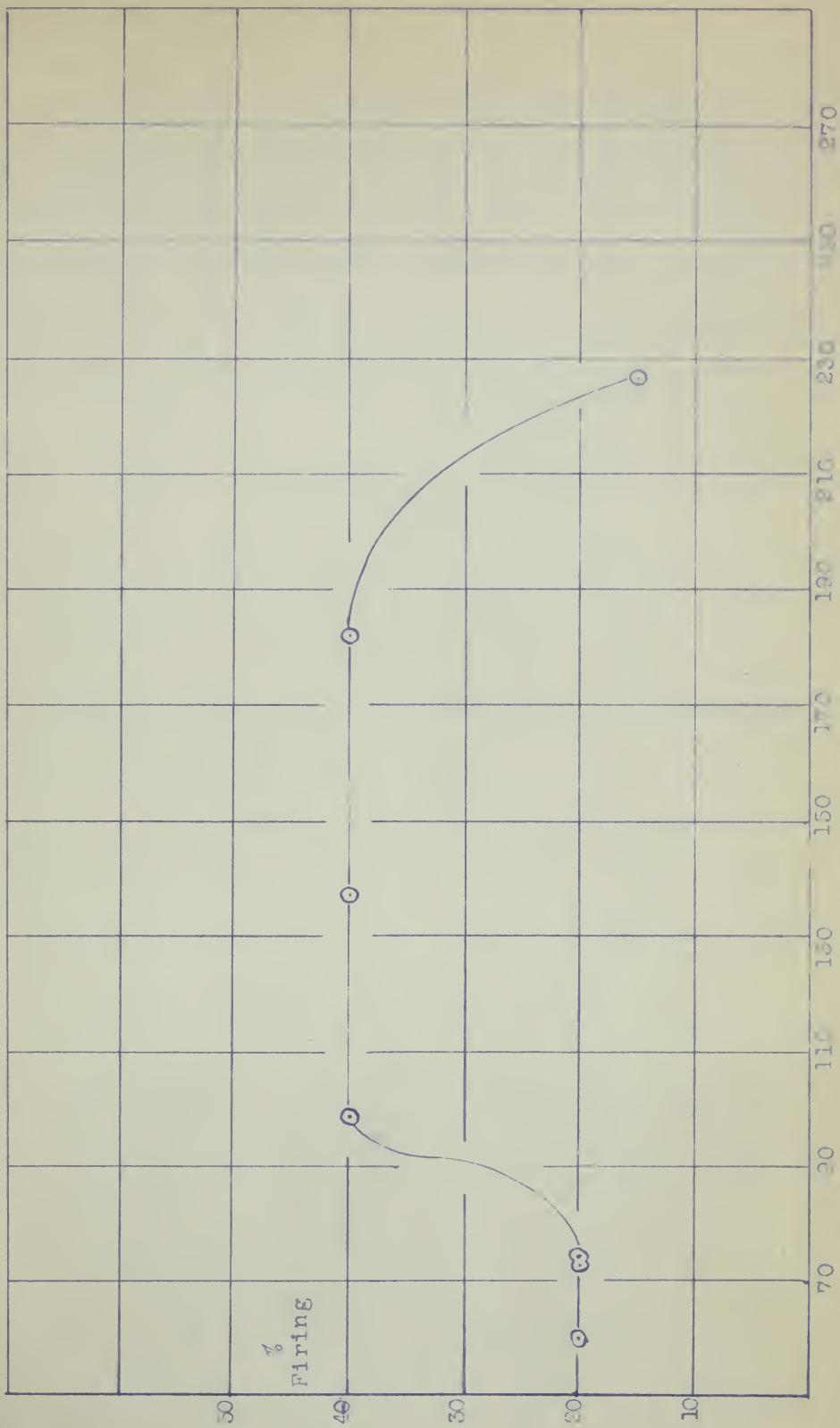


Fig. 8. Load pounds vs. Firing % Firing for line 66.5 cm. w.s. From 1150 tons.



rises quite sharply, remains horizontal over quite a range, then drops sharply. The points obtained were quite far apart. A more detailed investigation might show a maximum value. It is very probable that the maximum range (or value) would differ for various initiators. Some indication of this was obtained with Type II apparatus.

The falling weights and heights were varied with constant load. The results for stannous methylene-dinitramine are shown in Table XVI and plotted in Figure 9.

The first two results gave a slope (Fig. 9) which was expected for this sensitive compound. This compares well with Powell and Ubbelohde (22).

When higher weights were used the percentage detonation was lower in spite of the larger impulse. According to Taylor and Weale (6) this indicates deformation or a lack of rigidity.

There was no sign of deformation in the metal parts. They had been subjected to some 2000 impacts and would be strain hardened. The indentation in the anvil remained constant.

A lack of rigidity in the system would be expected at higher heights for the larger weights. But at



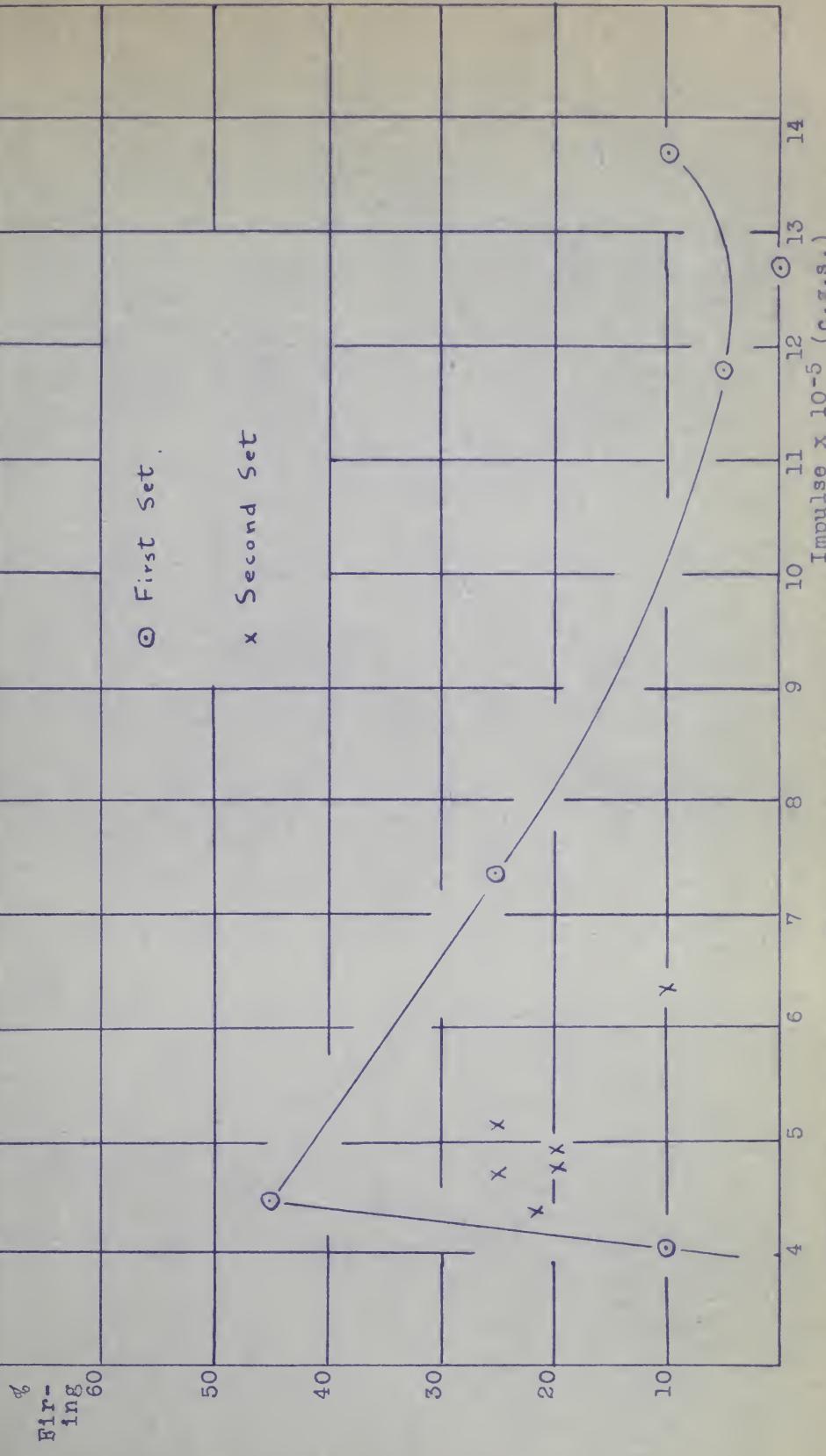


FIG. 9. Impulse vs. % Firing for Stannous Methylenedinitramine.



the heights used this should not be present. This is shown by the high values of  $e$  obtained for the larger weights. These were approximately 0.1 higher than values obtained with no sample at the same heights with Type I apparatus. Values of  $e$  are higher for a rigid system than for a non-rigid system.

Table XVI

Load 137 pounds.

<u>Weight</u>	<u>Height</u>	<u><math>e</math></u>	<u>K.E.</u>	<u>Impulse</u>	<u>% Firing</u>
66.6 gm.	119.4 cm.	0.384	$6.7 \times 10^6$	$4.5 \times 10^4$	40
66.6	99.8	0.375	$5.6 \times 10^6$	$4.1 \times 10^4$	12.5
130	69.3	0.535	$6.3 \times 10^6$	$7.4 \times 10^4$	25
225	50	0.674	$6.0 \times 10^6$	$11.8 \times 10^4$	5
225	61.6	0.631	$8.2 \times 10^6$	$12.8 \times 10^4$	0
225	69.8	0.643	$9.1 \times 10^6$	$13.8 \times 10^4$	10
66.6	138	0.376	$7.8 \times 10^6$	$4.8 \times 10^4$	20
66.6	138	0.352	$7.9 \times 10^6$	$4.7 \times 10^4$	25
66.6	152.2	0.354	$8.7 \times 10^6$	$4.9 \times 10^4$	20
66.6	163.5	0.354	$9.4 \times 10^6$	$5.1 \times 10^4$	25
66.6	118.3	0.361	$6.7 \times 10^6$	$4.4 \times 10^4$	20
130	62.6	0.392	$6.8 \times 10^6$	$6.35 \times 10^4$	10

It is proposed here that the inefficiency of the larger weights is not entirely due to a lack of rigidity in the system. There is another factor, namely,



the duration of impact. According to Rebiffe (23) the time of impact of hardened steel balls, of mass m and radius r, on a hard steel plate is proportional to  $\left(\frac{m^2}{r}\right)^{1/5}$  and to  $\left(\frac{1}{v}\right)^{1/5}$  where v is the velocity at impact. The mass is seen to be most important. In this system the range of weights used was large, whereas the range of velocities was quite small. To illustrate this compare the time of impact of the 66.6 gm. ball (radius 0.9 cm.) falling from 120 cm. with that of the 225 gm. ball (radius 1.45 cm.) falling from 60 cm. Assume the time of impact  $\propto \left(\frac{m^2}{r}\right)^{1/5} \cdot \left(\frac{1}{v}\right)^{1/5}$ . Velocity of ball from 120 cm = 485 cm per sec.  
" " " " 60 cm = 344 cm per sec.

For the 66.6 gm ball

$$\text{Time of impact } \propto \left(\frac{66.6^2}{0.9}\right)^{1/5} \cdot \left(\frac{1}{485}\right)^{1/5}$$

$$\propto 5.42 \times 0.298$$

$$\propto 1.62$$

For the 225 gm ball

$$\text{Time of impact } \propto \left(\frac{225^2}{1.9}\right)^{1/5} \cdot \left(\frac{1}{344}\right)^{1/5}$$

$$\propto 7.67 \times 0.344$$

$$\propto 2.64$$

Therefore the larger weights have a greater time of impact i.e. the impact compression of the explosive is slower than for small weights.



Starting with the 7th result in Table XVI the system shows a breakdown. The results are irregular. The values of e for the same weight and conditions shows a very noticeable drop (compare numbers 1 and 11, 3 and 12). This drop indicates a new lack of rigidity. The change is probably due to a breakdown of the concrete base under the base plate (see Figure 3). The rigidity of the base plate depends on the concrete beneath it and the tightness of the holding bolts. Concrete dust was observed around the boltholes in the base plate. A massive rigid base of iron or steel (such as used by Taylor and Weale (6), Powell and Ubelohde (22)) would overcome this difficulty. A base plate secured to the base independently of the outer retainer is also recommended.

Microscopic examination of negative results with Types II and III apparatus showed ice formation similar to that found with the friction apparatus. Stannous methylenedinitramine showed ice formation with pressure alone. This was found even at the smallest loads used. Mercury fulminate and lead azide showed no signs of icing with pressure alone over the entire range. These compounds required impact to form ice.

Stannous methylenedinitramine gave partial detonations with Types I and II apparatus but very few



with Type III apparatus. The compound does not possess the power to transfer the detonation wave from one spot to another. Mercury fulminate and lead azide did not show partials with any type of apparatus.



## A DISCUSSION OF THEORY

The results just presented are not conclusive.

In summary they indicate a number of effects associated with detonation.

1. An activation energy connected with the mechanical blow.
2. The dependence of detonation on impact (ft).
3. A relation between static pressure and impact sensitiveness.
4. The importance of time of impact (time occurs in impact, ft).
5. A parallel between impact and friction sensitiveness.

It is worth while to correlate these indications with what is already known of the detonation phenomenon, in a tentative theory of detonation. At the same time it will be pointed out where data is lacking, and what further work may be done.

All explosives are thermochemically unstable -- the reaction, explosive  $\rightarrow$  products, is exothermic (irrespective of whether an explosive is endothermically or exothermically formed from its elements). But there is no relation between this thermal instability and the compound's sensitiveness. Sutton (23) has suggested the



following criteria for a good explosive (high or initiating):

1. like atoms should be linked,
2. where unlike atoms are linked there should be small differences in electronegativity,
3. resonance in the molecule as a whole should be avoided.

The value of an initiator arises from (a) high sensitivity to mechanical impact (b) enough power to initiate explosion in another explosive. Both qualities do not necessarily occur in the same compound. High explosives possess only the second. Some compounds only possess<sup>s</sup> the first. Stannous methylene-dinitramine, for instance, has little or no power but great sensitivity. Lead azide and mercury fulminate possess both qualities. This is proven not only by the sand bomb test, but also in the impact test. No partials are observed for these two. If one part is initiated, all goes off. The tin salt, on the other hand, gives many partials.

Theoretically any thermodynamically unstable crystal should explode under favorable circumstances (activation energy). The principle question is why are some sensitive to mechanical impact while others are not. Seldom in explosives work do we meet with single crystals.



Rather, explosives are a large number of small imperfect crystals or crystallites. Any theory of detonation must take this into account when interpreting experimental data. The density of the aggregate is always less than that of the single crystal, and even under several hundred atmospheres it only approaches it. Thus lead azide crystal density  $D = 4.79$ , at 200 atmospheres per  $\text{cm}^2$   $D = 2.90$  and at 800 atmospheres per  $\text{cm}^2$   $D = 3.50$  (Muraour (7)).

A slow compression does not explode an initiator, but a fast one may. Even under slow compression, however, it is inconceivable that crystals will not be broken -- crushed and rubbed against each other, at some points, at quite a rapid rate; yet they do not detonate. This makes it difficult to accept the theory of Taylor and Weale, which is kind of surface reaction theory -- a making and breaking of bonds between crystals. Slow compression allows time for closer packing of the crystals so that the density approaches crystal density. At the same time, the increased packing means larger effective crystal surface presented to the faces of the hammer and anvil in the impact test. Thus, while the blow delivered to the anvil is kept constant, it is distributed over more crystal surface -- hence it is less effective. This is shown by experiments on the tin salt -- where beyond a certain pressure the sen-

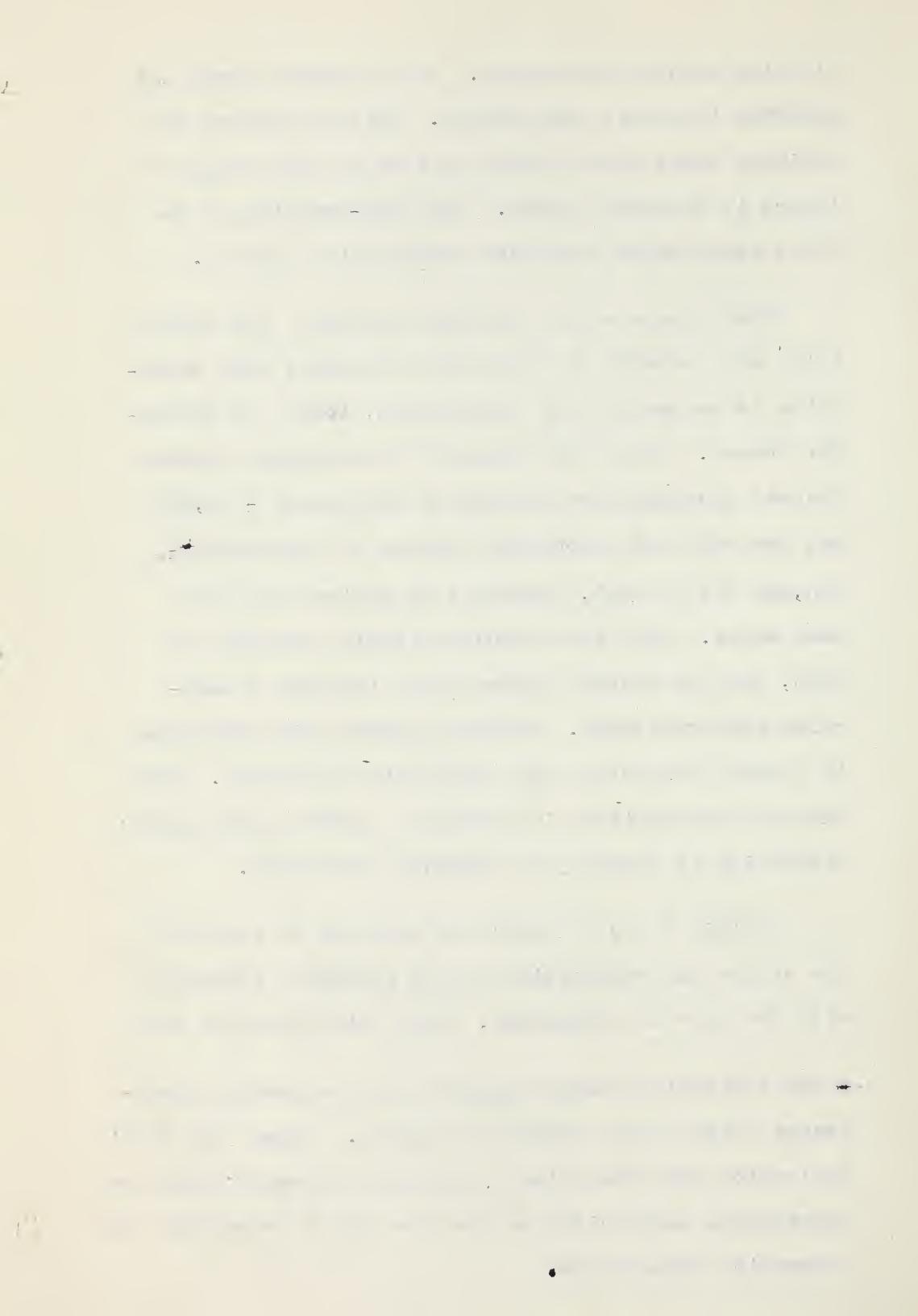


sitivity apparently dropped. But a certain amount of pressure increases sensitivity. This is because the ordinary loose powder soaks up some of the energy of impact in becoming packed. Thus pre-pressing in the first experiments gave more reproducible results.

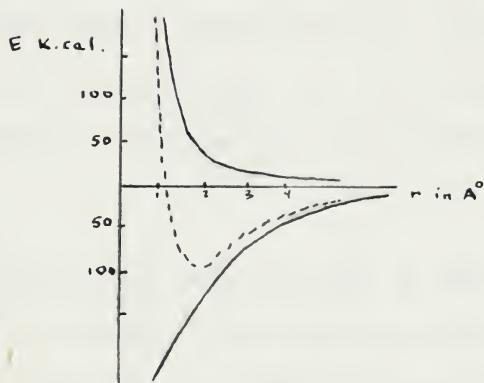
What occurs at the optimum pressure? The specificity of a crystal to detonation indicates that detonation is connected with interatomic, ionic or molecular forces. Garner and Gomm (25) distinguish between thermal decomposition (energy of activation = 50,000 cal per mol) and detonation (energy of activation\* = 150,000 cal per mol, corrected by Sutton (26)) for lead azide. The first involves single molecules of  $\text{PbN}_6$ , and the second (Sutton (26)) involves 3 molecules simultaneously. Sutton suggests that detonation is closely connected with crystalline structure. Pure thermal decomposition is probably a surface phenomenon; detonation is probably an internal phenomenon.

If this is so it should be possible to correlate the nature and composition of the internal structure with the ease of detonation. Most initiators are salt-

\* The activation energy suggested by the present experiments arises from mechanical impulse. Garner and Gomm's activation for detonation is measured by determining the temperature coefficient of the time lag to detonation at detonation temperatures.



like compounds -- usually a heavy metal cation linked with a complex anion. The nature of the pure electrovalent bond between oppositely charged ions has been expressed theoretically by Born, in the form of a potential energy curve.



This represents the energy of a molecule as a function of  $r$ , the distance between the atomic nuclei. At great distances an attraction operates based on Coulomb's law  $\frac{-e^2}{r}$ ; at smaller distances a repulsion  $+\frac{b}{r^n}$ , due to the closed electron shells (Pauli exclusion principle) comes into operation. Thus potential energy  $= \frac{b}{r^n} - \frac{e^2}{r}$  for oppositely charged ions.  $b$ ,  $\alpha$  and  $n$  are constants characteristic for each substance.  $n$  is of the order of 10 for the alkali halides.

The tensile strength of an electrostatically bound crystal should be determined largely by the attractive



force term. Joffe (27) found that if precautions were taken to avoid surface cracks, the tensile strength of a rock salt crystal actually was not far from the theoretical value, 200 kg. per mm.<sup>2</sup>. Compressibility data are used for calculating the value of the repulsive term; the equilibrium distance  $r_0$  will be determined largely from such data. Unfortunately, very little compressibility data are known for salts, except for the alkali halides. But certain generalizations can be made.

The character of a bond depends on the electronegativity of the atoms. The alkalies and alkaline earths give up electrons (8 electron shells) more effectively -- they are more electropositive than the heavy metals (18 electron shells). Thus the bonding of heavy metals has less electrostatic character and so is looser -- larger  $r_0$  values. This is born out by Richard's data (28).

Richards has correlated the tightness of the electrostatic binding (contraction) with the heat of formation of chlorides from the elements. Alkali and alkaline earth chlorides show large contraction and large heats of formation. The chlorides of the 18 electron closed-shell metals show small heats of formation, and contraction bonding. Thus, the heavy metal chlorides are more compressible.



Let us apply these generalizations to initiators and related crystals. Muraour (7) pointed out that the heavy metal salts of hydrazoic and fulminic acids were much more sensitive to impact than the corresponding alkali and alkaline earth salts (Table XVII). All are thermally unstable and their temperatures of thermal decomposition are much the same.

TABLE XVII

	<u>Ignition Temp.</u>	<u>Sensitivity (500 gm. wt. mm. fall)</u>
Sodium azide	280° C.	300 mm. (with 820 gm. wt.)
Sodium fulminate	150°	320
Lead azide	330°	225
Mercury fulminate	215°	75 - 100
Silver azide	290°	310
Silver fulminate	170°	140

X-ray crystallographic examination shows that for both the alkali azides and heavy metal azides (see Pauling (29) for  $\text{NaN}_3$ ,  $\text{KN}_3$ ,  $\text{AgN}_3$ ) the azide groups and the metallic ions are effectively in successive layers. There is no significant difference in the relative positions of the parts. The only significant difference then, is the fact that the heavy metals form bonds with less electrostatic or ionic characters -- looser -- more compressible.



This, along with the fact that thermal instability alone is not a criterion of sensitiveness, and that sensitiveness increases with rise in temperature (Taylor and Weale (6)) and so does compressibility (Bridgeman (30)) leads one to propose that sensitiveness to detonation is characterized by ease of compressibility or looseness of bonding in a thermochemically unstable compound. Contributing factor (to thermal instability) may be the fact that the heavy metals can exist in the free state on decomposition, whereas the alkali metals cannot.

How do these possibilities "explain" detonation? A mechanical blow does two things to a crystal (a) compression (b) subsequent recovery if the elastic limits are not exceeded (reversible). We propose that the first part is the important part. This has not been tested but experiments could be devised to do so.

TDS-1432

If compression is irreversible the body rearranges and if an explosive it may explode. Whether the compression is reversible or not will depend on (a) the magnitude of the blow, (b) the nature of the substance itself -- bonding, etc., (c) the time of impact. If a blow of a certain magnitude is slowly applied, ordinary compression spreading through the crystal, or even flow may occur. But, if applied rapidly enough, the blow may not be "absorbed" rapidly enough to prevent its breaking softer



bonds (Brittleness depends on rate of impact -- Houwink (15)). The alkali azides can absorb and spread such a blow more effectively than heavy metal azides and fulminates.



## A SUMMARY OF PROPOSED EXPERIMENTS

This thesis reports preliminary work on the subject. The work has suggested further experiments.

1. In the sand bomb test the iron wire bridge should be replaced by a platinum foil bridge to obtain a greater thermal impulse for salts such as stannous methylene-dinitramine.
2. The present base of the impact apparatus should be replaced by a massive iron or steel base. A hardened steel base plate should be fastened to the base by a number of independent bolts.
3. The rigidity of the system might be determined by determining the coefficient of restitutiuon over a wide range of velocities of the weights. A plot of these should give a straight line relationship for a rigid system. Where deformation takes place a change of slope of the line will occur. (Andrews, Phil Mag. 9 607 (1930)).
4. Tests should be made to determine whether the bounce (activation) effect is present in Types II and III apparatus. If it is present it could be investigated further by using two steel balls in successive impacts from different heights.
5. A wide range of compounds should be tested on both friction and impact apparatus to determine the relationship between the tests.
6. The "ice" formed should be examined under a polar-



izing microscope to follow the strains.

7. The effect of the time of impact should be investigated -- by the use of balls of different masses or methods involving a pendulum or magnetic forces.

8. Determine the optimum static pressures in impact sensitivity to see if there is a specific pressure for each explosive.

9. Determine whether compression or release is the important part of impact.



## BIBLIOGRAPHY

- (1) Davis - "The Chemistry of Powder and Explosives".
- (2) Compt. Rendu 1228 (1874).
- (3) Berthelot - "Explosives and Their Power".
- (4) Colver - "High Explosives" (1918).
- (5) Nernst - "Theoretical Chemistry" p.789 (1923).
- (6) Taylor and Weale, Proc. Roy. Soc. 138 92 (1932).
- (7) Muraour, H., Bull. Soc. Chim. 51 1152 (1932).
- (8) Taylor and Weale, Trans. Faraday Soc. 34 1000 (1938).
- (9) Carl, L.R., Jour. Franklin Inst. 230 75, 207, 355 (1941).
- (10) Miles, F.D., J. Chem. Soc. 2532 (1931).
- (11) Storm and Cope, U.S. Bur. Mines Tech. Paper 125.
- (12) Robertson, R., J. Chem. Soc. 1, (1931).
- (13) Hopkinson - Proc. Roy. Soc. 103 622 (1923).
- (14) Taylor and Rinkenbach, J. Franklin Inst. 204 369 (1927).
- (15) Houwink, R., "Elasticity, Plasticity and Structure of Matter" p.71 - (1937).
- (16) Bowden, J. - J. Applied Phys. 14 80 (1943).
- (17) Science Abstracts 2387 (1924).
- (18) Clark, Ind. Eng. Chem. 25 663 (1933).
- (19) Robinson, I.M. and Wright, G.F. - Report Proj. C.E. -12  
May 1942.
- (20) Dunstan and Goulding, J. Chem. Soc. 71 1264 (1900).
- (21) Urbanski, T., Z.f.g. Schiess und Sprengstoffwesen  
Feb. 1938 p.41-44.



- (22) Powell and Ubbelohde - A.C. 2641 S.E. 72.
- (23) Rebuffe, M.L., Compt. Rendu. 1230 (1936).
- (24) Sutton, L.E., Report - "The Relation of Some Recent Developments in the Thermochemical Theory to Explosive Research" 1941.
- (25) Garner and Gomm, J. Chem. Soc. 2123 (1931).
- (26) Sutton, T.C., Nature 133 463 (1934).
- (27) Joffe, A.F., "The Physics of Crystals" p.56-66 (1928).
- (28) Richards, T.W., Trans. Faraday Soc. 24 111 (1928).
- (29) Hendricks and L. Pauling, J.A.C.S. 47 2904 (1925).
- (30) Bridgeman, P.W., "The Physics of High Pressures"  
P.186 (1931).



APPENDIX DRAWINGS.



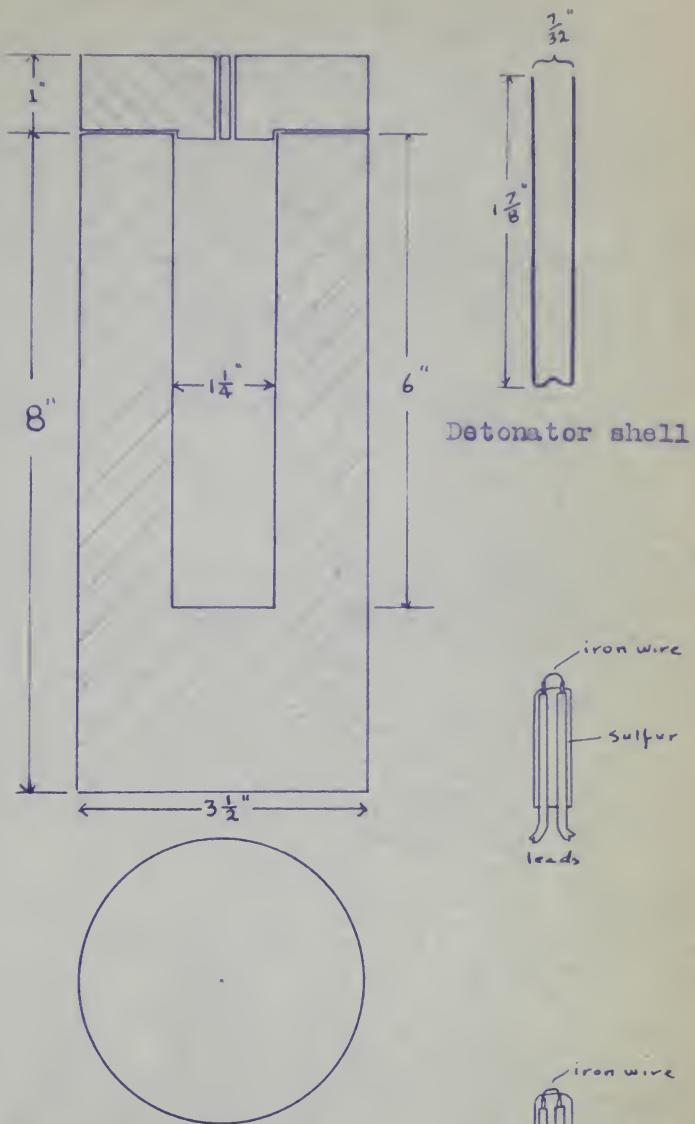
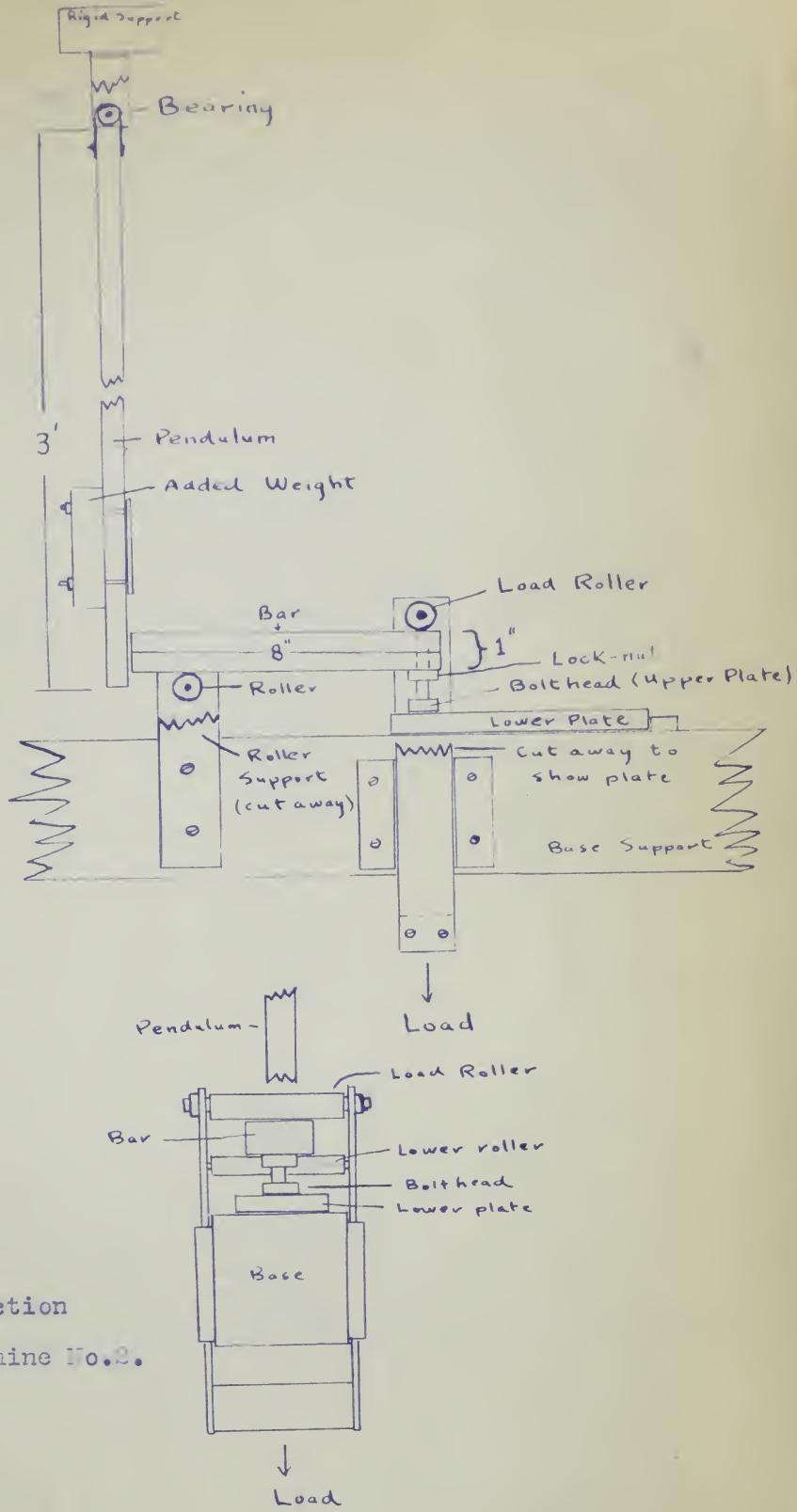


Fig. I. Sand Bomb.

Sulfur plugs.







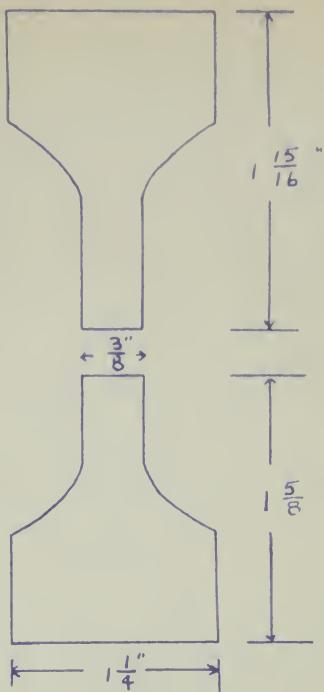
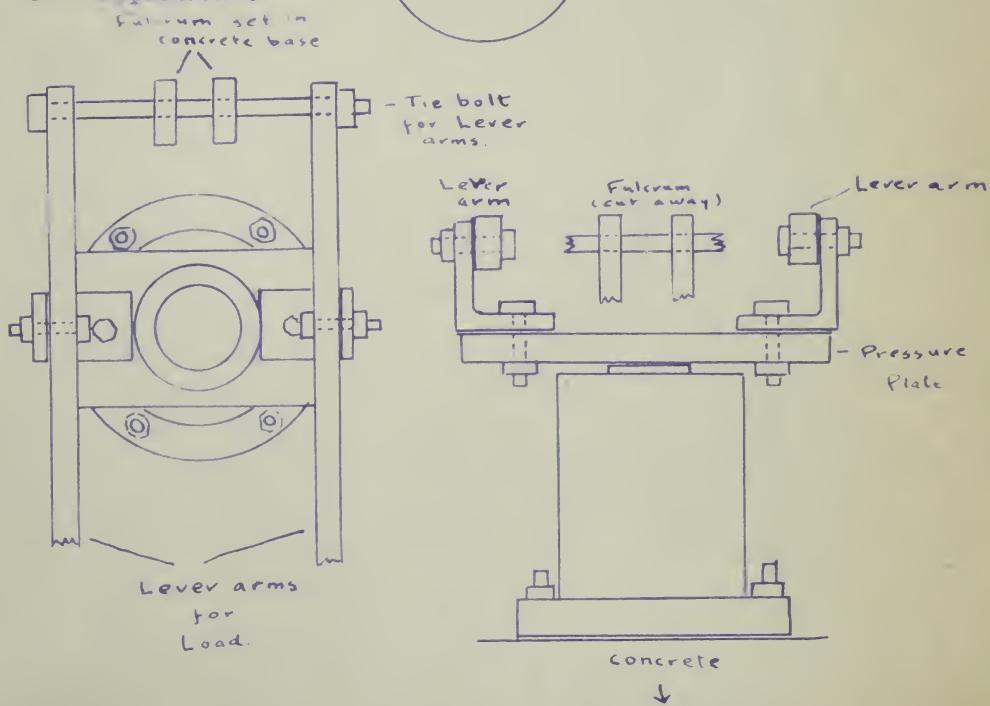


Fig. 6. Hammer and anvil.

Loading system  
of Types II and  
III apparatus.











**B29750**